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Mesogenic study of the H-bonded complexes of *N*,*N*-disubstituted aminophenylazo-(4)-1,3,4-thiadiazole with *p*-alkoxybenzoic acids

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A 2-diazenyl substituted 1,3,4-thiadiazole formed complexes with a series of *p*-alkoxybenzoic acid by intermolecular hydrogen bonding. The complexes were investigated by polarizing optical microscopy and differential scanning calorimetry to understand the resulting mesogenic behaviours. A study of the complex by powder XRD and molecular modelling was further undertaken to locate the position of hydrogen bonding.

1. Introduction

Azo dye molecules are attracting much attention in both academic and application areas [1, 2]; in particular, azo dyes have a useful dichroic ratio and are suitable for lower power consumption reflective liquid crystal devices [3]. In a guest–host system (GH), the dichroic dye is dissolved in a liquid crystal to give better reflectance [4]. In particular, three-layered GH systems with subtractive colour mixing of yellow, magenta, and cyan are expected to be used for developing full-colour reflective displays [5]. However, the solubility and phase transition temperatures of the GH systems present serious problems for use in device applications. Usually, the clearing temperatures vary with the components of the GH systems, and addition of the non-mesogenic dyes often causes instability of the liquid crystalline phase [6]. Dyes which are themselves mesogenic minimize this effect, and therefore azo dye liquid crystals are highly desirable as dopants.

Previously, we have successfully synthesized a series of crystalline yellow azo dye molecules containing an electron-donating amino functionality and an electron-withdrawing carboxylate group, as shown as structure **1** [7]. To obtain compounds with a magenta or cyan colour, i.e. to decrease the LUMO-HOMO energy gap of the molecules, it may be useful to synthesize compounds with stronger electron-withdrawing groups, such as CN or NO_2, to replace the carboxylate moiety. Although we can achieve this purpose by such a strategy, the diversity of the liquid crystalline molecules is limited to some extent, as the CN and NO_2 functional groups are short and no further attachments can be linked to them. Therefore we tried to reduce the LUMO-HOMO energy gap of the molecules by introducing the pyridine unit to replace the benzene carboxylate moiety; consequently the H-bonded complexes prepared from compound **2** and alkoxybenzoic acids were studied [8*a*, *b*]. However, the UV-visible absorption of **2** does not significantly vary from that of **1**. The main absorption of these compounds in CH_2Cl_2 is at about 410 nm. We thus further introduced the 1,3,4-thiadiazole ring into our azo dye system and studied the mesogenic behaviours of its H-bonded complexes with a series of *m*-alkoxybenzoic acids [8*c*]. The UV-visible absorption (λ_{max}) of compound **3** in dichloromethane occurs, as expected, about 466 nm. The primary result indicates that the thiadiazole ring does cause a significant red-shift of the UV-visible absorption and compound **3** may, as a result, be useful in optical applications. This encouraged us to study further its H-bonded oomplexes with a series of *p*-alkoxybenzoic acids, and the solubility of a new H-bonded complex in a host liquid crystal. Although the thermo-mesomorphic H-bonded complexes between pyridyl derivatives and carboxylic acids have previously been investigated [9], the corresponding study between the thiadiazole and benzoic acid derivatives is rare [8*c*]. Further study of

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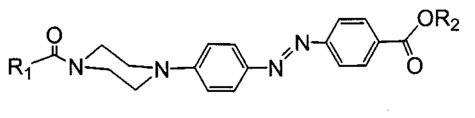
the corresponding mesogenic behaviour is thus worthwhile. The thermal properties of compound **3** were also further investigated, with results discussed in this paper.



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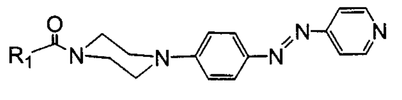

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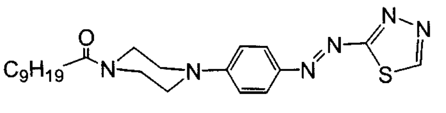

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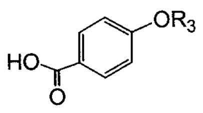

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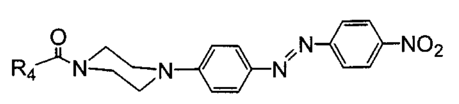
$R_3 = C_6H_{13}, C_8H_{17}, C_{10}H_{21}, C_{12}H_{25}$



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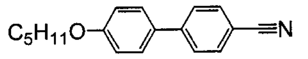

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2. Experimental

Chemicals used were commercially available from ACROS. *p*-Alkoxybenzoic acids **4** were synthesized by literature methods [9]. The azo dye **3** was prepared according to our previous procedure [8*c*] and its thermal stability was characterized by thermogravimetric analysis (Perkin-Elmer TGA 7). The UV-visible absorption (λ_{max}) of compound **3** was recorded using a HP 8453 UV-visible spectrometer. The hydrogen-bonded complexes S2N-*p*-AB*n* were prepared by dissolving the azo dye and benzoic acid derivatives in a 1 : 1 ratio in sufficient amounts of tetrahydrofuran (THF). The resulting solutions were then maintained in a fume hood for 48 h while THF was allowed to evaporate spontaneously. The resulting solids were ground and thoroughly blended. The mesogenic behaviours and phase transitions were characterized by polarizing optical microscopy (POM) and differential scanning calorimetry (Perkin-Elmer DSC 7 or DSC 6). Powder X-ray diffraction (XRD) patterns were obtained from a Siemens D-5000 X-ray diffractometer equipped with a TTK 450 temperature controller and Cu radiation with the wavelength $\lambda = 1.5406$ Å. A semi-empirical calculation was carried out by CAChe program (version 4.4), which was provided by Fujitsu (Japan).

3. Results and discussion

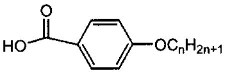
As mentioned previously, the UV-visible absorption (λ_{max}) of compound **3** occurs at about 466 nm (in CH_2Cl_2), and shows a more significant red-shift than that of compound **5** (R_4 = Me, 437 nm in EtOH) [10]. Incidentally, the mesogenic behaviour of azo dye derivative **5** ($R_4 = C_9H_{19}$) was unsatisfactory in our earlier study; it is monotropic and only shows a SmA phase in the range 140–138°C on cooling. Compound **3**, however, has better mesogenic behaviour; it shows an enantiotropic SmC phase with a range of about 50° on cooling (table 1). In particular, it is reasonably stable, and only starts to decompose at about 280°C under investigation by thermogrametric analysis. The alkoxybenzoic acid derivatives **4** (n = 6, 8, 10, 12) show enantiotropic nematic and (or) SmC phases (table 2) [9*b*, 11]. With short alkyl chain lengths, the nematic phase is observed; with longer chains, the SmC phase is also observed.

The H-bonded complexes S2N-*p*-AB*n* show an enantiotropic SmC phase. The mesogenic behaviours of the

Table 1. Phase transition temperatures (°C) and corresponding enthalpies (J g^{-1}), in parentheses, of hydrogen-bonded complexes from a 1 : 1 molar ratio of compound **4** (n = 6, 8, 10, 12) and azo dye **3**. Determined by 2nd scans of DSC using Perkin Elmer DSC-7 at a heating and cooling rate of 5°C min^{-1} between 45 and 170°C. Abbreviations: Cr = crystalline, SmX = unidentified phase, SmC = smectic C phase, I = isotropic liquid.

Azo dye **3**	Cr	$\underset{100.3(38.6)}{\overset{144.7(38.1)}{\rightleftharpoons}}$	SmC	$\underset{153.6(9.2)}{\overset{155.4(4.6)}{\rightleftharpoons}}$	I
S2N-*p*-AB6	SmX	$\underset{88.2(0.3)}{\overset{92.6(39.4)}{\rightleftharpoons}}$	SmC	$\underset{139.6(8.7)}{\overset{152.4(16.5)}{\rightleftharpoons}}$	I
S2N-*p*-AB8	SmX	$\underset{88.5(0.4)}{\overset{91.6(22.4)}{\rightleftharpoons}}$	SmC	$\underset{152.7(8.7)}{\overset{156.4(12.8)}{\rightleftharpoons}}$	I
S2N-*p*-AB10	SmX	$\underset{87.8(0.8)}{\overset{87.2(14.7)}{\rightleftharpoons}}$	SmC	$\underset{156.0(7.8)}{\overset{159.9(9.1)}{\rightleftharpoons}}$	I
S2N-*p*-AB12	SmX	$\underset{88.5(0.6)}{\overset{80.0(6.1)}{\rightleftharpoons}}$	SmC	$\underset{157.3(13.1)}{\overset{162.3(14.2)}{\rightleftharpoons}}$	I

Table 2. Phase transition temperatures (°C) and corresponding enthalpies ($\mathrm{J\,g^{-1}}$), in parentheses, of **4** ($n=6$, 8, 10, 12). Cr = crystalline, SmX = unidentified smectic phase, SmC = smectic C phase, N = nematic phase, I = isotropic liquid.



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$n=6$	$\mathrm{Cr} \xrightleftharpoons[89.5(53.1)]{104.5(54.5)} \mathrm{N} \xrightleftharpoons[145.1(8.6)]{148.6(9.7)} \mathrm{I}$
$n=8$	$\mathrm{Cr} \xrightleftharpoons[48.1(48.3)]{73.9(5.7)} \mathrm{SmC} \xrightleftharpoons[91.2(44.8)]{98.3(45.8)} \mathrm{N} \xrightleftharpoons[137.89(7.2)]{140.0(7.2)} \mathrm{I}$
$n=10$	$\mathrm{Cr} \xrightleftharpoons[70.9(78.3)]{85.9(75.9)} \mathrm{SmX} \xrightleftharpoons[89.4(41.6)]{96.0(41.7)} \mathrm{SmC} \xrightleftharpoons[118.2(9.5)]{121.8(5.7)} \mathrm{N} \xrightleftharpoons[137.1(5.9)]{140.8(8.8)} \mathrm{I}$
$n=12$	$\mathrm{Cr} \xrightleftharpoons[61.3(10.7)]{75.6(10.4)} \mathrm{SmX1} \xleftharpoondown[76.1(1.4)]{} \mathrm{SmX} \xrightleftharpoons[82.9(17.7)]{89.2(26.1)} \mathrm{SmC} \xrightleftharpoons[118.5]{122.3} \mathrm{N} \xrightleftharpoons[120.3^{b}]{124.5^{a}} \mathrm{I}$

[a] The peaks are overlapped and their total enthalpy is 20.6 $\mathrm{J\,g^{-1}}$.

[b] The peaks are overlapped and their total enthalpy is 14.5 $\mathrm{J\,g^{-1}}$.

complexes S2N-*p*AB*n* are similar to those of the acids **4**, and induced through intermolecular hydrogen bonding. The SmC phase of the azo dye **3** and S2N-*p*-AB*n* was characterized by the broken focal-conic texture coexisting with the schlieren texture and their low viscosity through POM. To investigate the miscibility of S2N-*p*-AB*n* in a host liquid crystal, compound **6**, prepared according to the literature [12], was mixed with a representative sample of S2N-*p*-AB8 (9/1, w/w) to give mixture **7**, and the mesogenic behaviours of both were investigated as shown in table 3. Compound **6** and mixture **7** show an enantiotropic nematic phase, characterized by schlieren textures and their low viscosity. The nematic range for **6** is about 15° on heating and 40° on cooling. The nematic range for mixture **7** is better; it even shows a nematic phase at room temperature on cooling, which is very important for optical applications. Additionally, no phase separation was observed for mixture **7** under POM.

Table 3. Phase transition temperatures (°C) and corresponding enthalpies ($\mathrm{J\,g^{-1}}$) of compound **6** and mixture **7** (mixture **7** = 1/9 molar ratio of S2N-*p*-AB8/**6**).

Compound **6**	$\mathrm{Cr} \xrightleftharpoons[30.1^{a}]{52.3(134.9)} \mathrm{N} \xrightleftharpoons[67.0(2.3)]{68.0(1.5)} \mathrm{I}$
Mixture **7**	$\mathrm{SmX} \xrightleftharpoons[21^{a}]{30.4^{a}} \mathrm{N} \xrightleftharpoons[59.1(0.5)]{62.3(0.7)} \mathrm{I}$

[a] The phase change temperature was determined by POM.

The SmC phase of S2N-*p*-AB*n* was further supported by the XRD study of a representative complex S2N-*p*-AB8. The *d*-spacing distances (the *Z* component of an extended molecular length) of the complex S2N-*p*-AB8 from the XRD study in the SmC phase are 34.68 Å at 100°C, 35.20 Å at 80°C and 35.77 Å at 60°C, as observed during cooling. It is suggested that the angle θ between *Z* (Cartesian axis) and the liquid crystalline axis in our case does not change significantly while the temperature is varied. Additionally, the greater vibration of the molecules at higher temperature in the solid state results in the gap between the molecular layers becoming closer, and thus the *d*-spacing decreases gradually as the temperature increases. Also, the X-ray pattern in the SmC range shows only a sharp reflection in the small angle region, suggesting a smectic layer structure without regular arrangement in the intralayers.

To understand the molecular interactions between the azo dye **3** and acid derivatives **4**, the partial charge of the representative complex S2N-*p*-AB8 was calculated by the CAChe program. The complex S2N-*p*-AB8 was optimized by performing a geometry calculation in mechanics using augmented MM2 parameters. Part of the charge distribution of the thiadiazole ring and the carboxylate moiety of the complex S2N-*p*-AB8 is shown in the figure. The partial charge for N1 (−0.071) in the 1,3,4-thiadiazole ring is more negative than that of N2 (−0.029). Additionally, the charges for H1 and H2 are all partially positive and calculated to be 0.270 and 0.235, respectively; the partial negative charge for O2 is −0.461. We thus suggest that hydrogen bonding can occur on the N1-H1 and O2-H2 pairs. The distance between N1 and H1 is calculated to be 2.29 Å; and the distance between H2 and O2 is calculated to be 2.63 Å. This implies that interaction between the acid **4** ($n=8$)

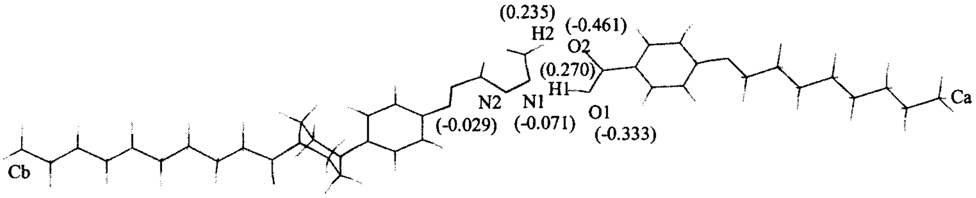

Figure. The distance between the N1 and H1 is calculated to be 2.29 Å. The distance between H2 and O2 is calculated to be 2.63 Å. The energy of complex S2N-*p*-AB8 is calculated to be 21.89 kcal mol^{-1}, and the energies of the corresponding compound **4** and azo dye **3** are respectively calculated to be -6.12 and 29.88 kcal mol^{-1} by MM2. The interaction energy is thus lowered by -1.87 kcal mol^{-1}. The value in parenthesis is the partial charge of the corresponding atom.

and azo dye **3** is quite possible, and the energy of the system is accordingly lowered by -1.87 kcal mol^{-1} (see the figure).

Significantly, the distance between Ca of **4** and Cb of **3** ($n=8$) is calculated to be 39.32 Å, which is much longer than the *d*-spacing obtained from the XRD study (36.23 Å at 25°C). On the basis of the layer distance from the XRD study and the length of the fully extended molecule from molecular modelling, the angle θ between Z and the molecular axis is calculated to be 22.87°. As the simulation of the molecule was carried out in vacuum, the optimized conformation is similar to that of the molecule in the gas phase. However the polarity of the complex S2N-*p*-AB8 can be reasonably applied to intermolecular interaction in the solid state in our case, as the polarity of the molecule should maintain consistency in the liquid, solid, and gas phases. The calculated H-bond distances between the acids **4** and the azo dye **3** may be greater than those in the complexes in the real situation, as the vibration of the molecules should be smaller in the solid state. However the small variation should not change our conclusion.

In conclusion, this work presents a successful approach to the formation of mesogenic heterocycle-containing azo dye complexes through intermolecular hydrogen bonding. This approach may open up another useful azo dye liquid crystal area. Mesogenic behaviour in other heterocycle-containing azo dyes with a narrower HOMO-LUMO energy gap may be brought about similarly.

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